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GROWTH AND STUDY OF NONLINEAR OPTICAL MATERIALS FOR FREQUENCY CONVERSION DEVICES WITH APPLICATIONS IN DEFENCE AND SECURITY

Vladimir Tassev, Michael Snure, Shivashankar Vangala, Martin Kimani, and Rita Peterson

Optoelectronics Technology Branch
Aerospace Components & Subsystems Division

Peter Schunemann

BAE Systems

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Vladimir Tassev, Michael Snure, Shivashankar Vangala, Martin Kimani, and Rita Peterson (AFRL/RYDH)
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Air Force Research Laboratory, Sensors Directorate
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Air Force Materiel Command, United States Air Force

BAE Systems
95 Canal Street
Nashua, NH 03061

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14. ABSTRACT

A series of nonlinear materials including GaAs, GaP, and ZnSe have been examined to determine their suitability for non-linear frequency conversion devices (FCD) and more specifically their use as high power, compact and broadly tunable IR and THz sources for applications in defense and security. The more mature GaAs was investigated to reveal the causes for the optical losses that restrict achievement of higher conversion efficiency in quasi phase matched FCD. The efforts to develop simple, cost effective techniques for fabrication of orientation patterned (OP) templates and to optimize the subsequent thick growth on these templates are presented.

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Growth and study of nonlinear optical materials for frequency conversion devices with applications in defence and security

V. Tassev[*a], M. Snure[a], S. Vangala[a,b], M. Kimani[a], R. Peterson[a] and P. Schunemann[c]
[a]Air Force Research Laboratory, Sensors Directorate, Wright Patterson AFB, OH 45433 USA
[b]Solid State Scientific Corporation, Hollis, NH 03049 USA
[c]BAE Systems, Nashua NH 03061 USA

ABSTRACT

A series of nonlinear materials including GaAs, GaP, and ZnSe have been examined to determine their suitability for non-linear frequency conversion devices (FCD) and more specifically their use as high power, compact and broadly tunable IR and THz sources for applications in defense and security. The more mature GaAs was investigated to reveal the causes for the optical losses that restrict achievement of higher conversion efficiency in quasi phase matched FCD. The efforts to develop simple, cost effective techniques for fabrication of orientation patterned (OP) templates and to optimize the subsequent thick growth on these templates are presented. Epitaxial growth of thick OPGaP on OP-templates resulted in average growth rates of 50-70 μm/h in up to 8-hour long growth experiments. High optical layer quality was achieved by suitable control of the process parameters. The optimal orientation of the pattern was determined and used as essential feedback aiming to improve the template preparation. This led to the production of the first 300-400 μm thick device quality OPGaP. Efforts to suppress the parasitic nucleation during growths with longer duration or to achieve thicker layers by a 2 step growth process were also made. The main challenge with the newer candidate, OPZnSe, was to establish suitable regimes for hydrothermal growth on plain (001) ZnSe seeds previously grown using chemical vapor deposition. Two different temperature ranges, 330-350ºC and 290-330ºC, were investigated. The mineralized concentration was also manipulated to accelerate the growth in (111) direction and, thus, to improve the growth in (001) direction. The next material on the line is GaN. The traditional HVPE approach will be combined with a growth at low reactor pressure. Growths will be performed in the next sequence: growth on thin GaN layers grown by MOCVD on sapphire wafers, growth on half-patterned GaN templates with different orientations and, finally, growth on OPGaN templates.

Keywords: hydride vapor phase epitaxy, nonlinear optical materials, quasi-phase matching, orientation patterned templates, frequency conversion devices, laser sources in the mid IR and THz region

1. INTRODUCTION

The successful implementation of several innovative ideas such as introducing the new two-color broadband detector materials (HgCdTe) that cover both atmospheric windows of transparency (2 – 5 and 8 – 12 μm) and replacing the spin scanning of the signal coming from the target with the more efficient confocal or "rosette" scanning has resulted in a great advancement in the IR seeking missile development—practically the focal-plane-array sensor of such a missile now has the sensitivity of a digital camera CCD. Taking further the advantages from areas such as optical communications and signal processing the contemporary heat seeking missiles are rather flying computers—they cannot be fooled easily but can see the target in fog and clouds and even communicate with the shooting station to confirm the origin of the target. Such missiles can be fired from either air-to-air or ground-to-air systems, including man-portable-air-defense (MANPAD) systems. Unfortunately more than a half-million MANPADS's have been produced worldwide in the last 2-3 decades and are readily available on the market at a reasonably low price. They are highly efficient and easy to use, i.e. do not require well-trained military personnel. Currently the major approach to aircraft protection is still through the passive distraction of the approaching missile by multiple flare decoys. This relatively low efficient approach is the only affordable way for mass protection of military aircrafts while civilian aircrafts are usually not protected. Obviously, the IR countermeasure development is a step behind the heat seeking missile development, which means

*vladimir.tassev@wpafb.af.mil, phone (1) 937-528-8995

that the distance should be shortened as soon as possible. The modern concept is a protection based on an active communication protocol between the IR countermeasure and the approaching missile. Such a protocol requires compact, high-brightness, tunable, and room temperature operating laser sources in the mid IR, which still do not exist at the moment. This single example of the urgent need for such sources does not exclude that such devices radiating in the IR and THz region will be also greatly sought in a wide variety of other military (laser radar, IR communications) and commercial applications: in security (scanners and remote sensing of chemicals—including explosives— and biological agents, in industry (gas sensing, leak detection, pollution monitoring, process control), in science (IR and THz spectroscopy) and in medicine (medical images, biopsy-free cancer cell detection).

One would be amazed by the great number of laser sources (http://en.wikipedia.org/wiki/List_of_laser-types) developed since 1960 when Theodore Maiman demonstrated at Hughes Research Labs the first ruby laser. However, -looking at the IR and THz region one will also be surprised by the small number of available direct sources in this frequency ranges:

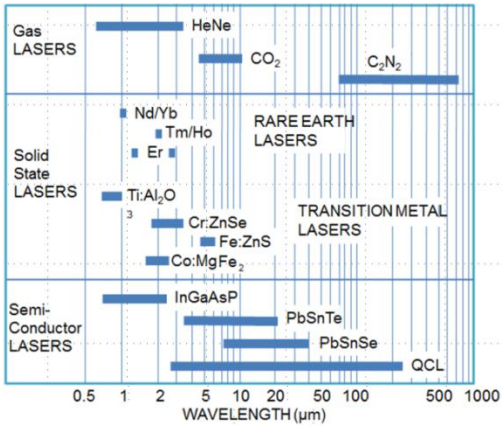


Figure 1. Current laser sources available in the IR and THz (http://en.wikipedia.org/wiki/Infrared_lasers).

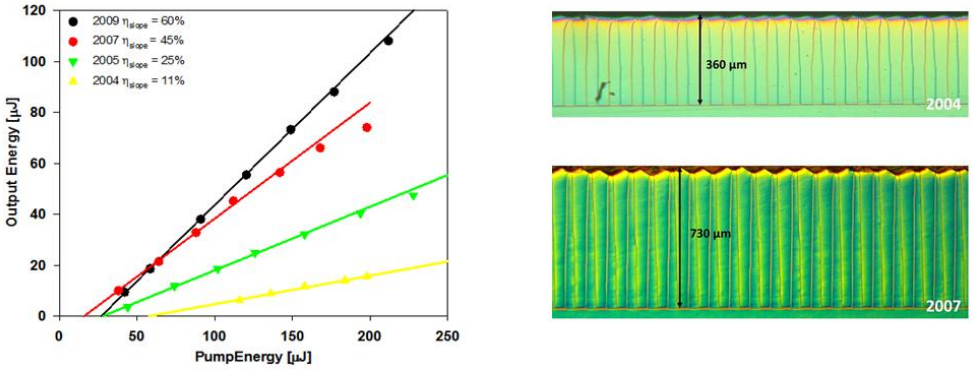
At first glance one can see that the quantum cascade lasers (QCLs) with their wide range of radiation are great for the purpose. However, QCLs are hardly tunable, with low conversion efficiency and typical output power in the range of 0.5 - 5 W, as their performance strongly deteriorates with the temperature. The next candidates that cover both atmospheric windows of transparency are sources based on some of the ternary lead salts. These sources, however, produce only mW of output power. They are tunable over only a few nanometers and require cryogenic temperatures to operate. In retrospect, the efforts to develop laser sources in IR and THz region, actually, start with the evaluation of a great variety of binary and ternary semiconductors [1] as direct sources. These binary and ternary semiconductors were successfully incorporated in IR countermeasures back in the mid-90s. However, they were expensive (according to some public domains the prices are in the range of $1.5M – $6.0M), required complex mechanics and had Jammer-to-Signal ratio (J/S) as low as 2:1 to a maximum of 50:1 (For a comparison the expectations for the next-generation IRCMs are for J/S in the range 300:1 – 2000:1). The inability to achieve the needed frequencies and power pushed researchers to seek alternative approaches based on wave mixing processes within a nonlinear medium. One of the most promising approaches is to convert the frequency of an available pump laser into the wavelength of interest via a nonlinear material. Initially employing bulk birefringent phase-matching (BPM) crystals [2], the idea was extended to compensating the phase velocity dispersion by using the quasi-phase matching (QPM). QPM provides the advantage of engineered phase matching that can be designed to match any frequency within the transparency range and in a direction to coincide with the largest element of the $\chi^{(2)}$ tensor. The first practical realization of such a structure was in the ferroelectric periodically-poled $LiNbO_3$ (PPLN). However, soon it became clear that due to its strong intrinsic absorption the usage of PPLN is limited to wavelengths shorter than 4 μm [3]. In non-ferroelectric materials QPM can be achieved by spatially inverting the nonlinear susceptibility. Initially this was done through alternating the orientation of wafers in a stack [4]. However, high optical losses, observed at the wafer interfaces, and the small layer thickness that is needed to satisfy the QPM conditions made these approaches unsuitable for practical devices. The attempts to grow on the edge of the stack solved the first issue, but not the second one. The advance in the planar technology adopted from the microelectronic industry, made possible the practical realization of thin microstructured materials for QPM interaction. The last step to the realization of QPM was to grow a thick enough layer on the thin template while maintaining the periodic orientation of the initial template pattern. GaAs with its broad IR transparency, high nonlinear optical susceptibility and mature growth technique [5] is an example of a successful QPM approach. However, OPGaAs is still

not the perfect material due its high two-photon absorption (2PA) in the convenient pumping range 1–1.7 μm [7]. Compared to GaAs, the same structured GaP has a negligible 2PA in the same region, with comparable nonlinear susceptibility, higher thermal conductivity, lower thermal expansion coefficients, lower photorefractive index and broad transparence that starts conveniently in the visible region [8]. These factors have made GaP one of the most promising QPM materials today. The rapidly increasing interest led to the design of the first GaP FCD based on stacked GaP wafers [9] and to the first demonstration of QPM parametric fluorescence in periodically inverted GaP [10]. It turned out, however, that a number of issues have to be solved first. For example, the OP template preparation process cannot be one-to-one copied from GaAs because of the absence of a suitable GaP etch stop material [11]. The hydride vapor phase epitaxial (HVPE) growth [12]—the only growth approach with proven capability of producing apertures large enough for high power applications—provides much slower growth rates [13] compared to GaAs and often results in poor crystalline quality [14]. In addition, all available n-type GaP samples have an absorption band between 2-4 μm [15, 16], which would be a big problem for the seeking IRCM applications.

This article aims to highlight the study of OP materials conducted at AFRL in the last several years, not as a snap shot but as a progressing process. Thus §2 shows the current progress in the mature OPGaAs research is discussed. §3 summaries the efforts to resolve some of the specific issues with GaP, which finally resulted in the first device quality 400 μm thick OPGaP. Last §4, dedicated to the future directions of this research, shows the results from the study of other promising nonlinear materials and growth approaches and expresses the team's belief that this research should be diversified to other materials and growth approaches.

2. RECENT PROGRESS IN OPGaAs STUDY

The interest of AFRL in QPM materials dates back to the mid 70's with the works of Szilagyi, Hordvik and Schlosberg [17], who describe a series of experiments with a stack of GaAs plates with alternating polarity, ordered at a Brewster angle for frequency doubling of laser radiation at 10.6 μm. The interest in the QPM GaAs, grown by HVPE on OPGaAs templates, was resumed nearly 30 years later with the advancements of the technology for fabrication of these engineered microstructured materials. As a consequence a rapid and continuous increase in the output power (Fig. 2-a), linked to the increase of the QPM structure thickness and improvements in the domain fidelity (Fig. 2-b) occurred.



(b)

Figure 2. Output energy as a function of the pump energy (a); improvements in domain fidelity and layer thickness increase (b).

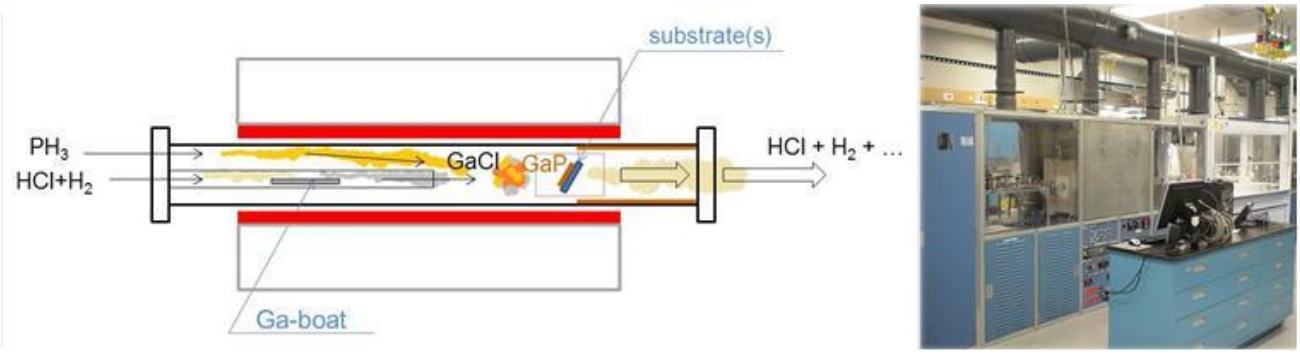
Despite these improvements, however, the conversion efficiency of these devices was still lower than the expected—a fact that is difficult to explain with the GaAs intrinsic properties. Continued research on the "hidden" reasons for scattering (twinning) and absorption (native and impurity generated absorption centers) revealed important findings [18]. The concept that the atomic bonds at the antiphase boundaries are rather monoatomic, i.e. Ga—Ga and As—As, than Ga—As bonds, was confirmed using High-Angle Annular Dark-Field (HAADF) imaging. From TEM cross sectional images twinning was observed as the primary defect in both domain orientations. Point defects were explored in detail as a key contributor to optical absorption losses. Plain GaAs and OPGaAs were grown and studied by Hall measurements, SIMS depth profiling, and cathode luminescence (CL). It was found that Si impurities are the primary source of donors, while V_{Ga} are identified as the primary source of acceptors. To increase CL and SIMS detectability the samples were intentionally doped with Si. Study of the OP material indicated that there is a significant difference in the defect

concentration in regions with different crystallographic orientation, i.e. generating defects and capturing impurities is an orientation dependent process. Si-concentration in [001] oriented domains, for example, is higher than in domains with [00$\bar{1}$] orientation. Similarly, CL indicated that when a (111) facet forms near the antiphase domain boundaries the absorption of Si on (111)B surface is weaker than on (001) or (00$\bar{1}$).

3. RECENT PROGRESS IN OPGaP STUDY

3.1. Experimental procedures

The HVPE growths of GaP were performed in a hot wall horizontal reactor customized for low pressure operation (Fig. 3). The 3-inch diameter quartz tube was heated in a 3-zone resistive furnace. Quartz boat with metal Ga was placed in the first zone. HCl passing the molten Ga formed GaCl and delivered it to the middle (mixing) zone where GaCl meets for the first time the peripheral (outer) PH_3 flow. The substrate was placed in the third (growth) furnace zone. High purity H_2 was used as a carrier gas in both inner and outer flows to dilute the precursors and to deliver the reactant species. Growth conditions such as total gas flow less than 250 sccm, substrate temperature in the range of 705–758°C and reactor pressure less than 10 Torr resulted in fast, high quality, thick highly reproducible growth. Three different types of substrates, plain (bare) GaP wafers, half-patterned (HP) and OP templates were used. The OP-templates were fabricated by a sub-lattice inversion MBE assisted process and by a wafer fusion (bonding) technique. "On-axis" (100) GaP wafers and wafers with 4° miscuts towards (111)B were used to fabricate the templates. The stripes of the patterns were oriented along either [011] or [01$\bar{1}$] direction. More details about these patterning techniques are given in [19, 20].



(a) (b)

Figure 3. Schematic diagram of the HVPE growth of GaP (a); one of the HVPE reactors (b).

Images of the surface morphology and cross sectional images were made by Nomarski, AFM and SEM. The structural quality was determined by high resolution XRD using omega-two theta rocking curves of (004) plane. Electrical (mobility and carrier concentration) and optical (IR transmission and absorption) properties were evaluated using RT Hall measurements, Cary 5000 spectrophotometer and Thermo-Nicolet FT-IR. The presence of different elements and their distribution were determined by Energy-dispersive X-ray (EDX) spectroscopy.

3.2. Results

3.2.1. Growth on plain GaP wafers

By optimizing growth parameters the growth rate on plain, HP and OP samples was increased from 70 µm/h (in 2010) to 100 µm/h (in 2013) for 1-hour growth duration (Fig. 4). This allowed growth experiments to be extended to 6 – 8 hours. The growth was found to reduce with time due to parasitic growth on the reactor walls. After 4 hours of growth, however, the deposition rate levels off at 45 µm/h.

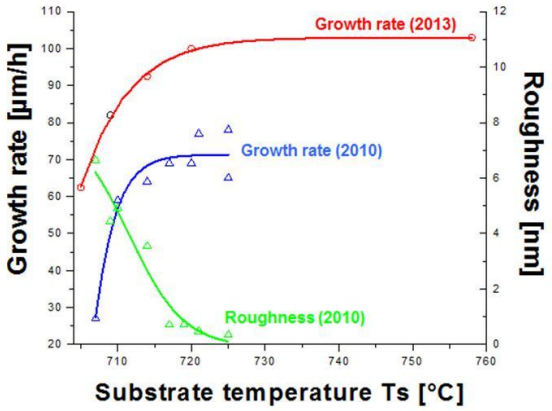
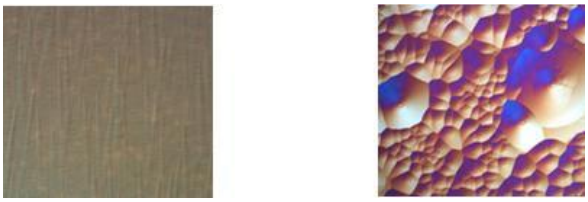


Figure 4. Growth rate and layer roughness as a function of the substrate temperature in 2010 and 2013.

At about 725 °C the growth rates reaches a maximum value, which does not change as the temperature was increased to 758 °C (2013). However, beyond 725 °C (where the roughness has a minimum) the roughness starts rapidly to increase, i.e. the surface morphology starts to deteriorate, which means that there is no sense to attempt growths at substrate temperatures higher than 725 °C. The V/III ratio for this series of experiments at different growth temperatures was constant and equal to 2.25. This comes from previously conducted experiments at different V/III ratios but a constant temperature of 725 °C. These experiments showed that to have a growth at 725 °C the V/III ratio must be in the range 2.03 – 4.46, as the growth rate had a maximum at V/III ratio of 2.25. In this range the layer roughness seemed to increase gradually, i.e. at 2.03 we got smooth surface morphology at low growth rate, while at 4.46 the surface was rough with the growth rate being low. Another growth parameter that might have strong impact on the growth rate and layer quality that we have not yet studied is the reactor pressure. Detailed analyses of the pressure impact in case of GaAs can be found in [22] and [23].

Another factor with great importance for the growth rate and the surface morphology is the substrate orientation. Growths were performed on "on-axis" (100) GaP and on (100) GaP with 4° miscut towards (111)B. The results indicated that the growth on misoriented wafers resulted in a smooth hillock-free surface morphology due to the great number of sites offered at the atomic terraces for the species approaching the growing surface to adhere. The growth rate was also about 40 % higher (Fig. 5-a). In contrast, growth on "on-axis" wafers resulted in morphology populated with a great number of hillocks whose widths and heights vary in a wide range (Fig. 5-b). The difference in surface morphology can be attributed to the higher number of atomic steps available for step flow growth on the 4° misoriented substrate. On a flat surface, where the density of step edges is less than the surface diffusion length of adatoms, islands will begin to nucleate randomly on the surface or at defect sites such as screw dislocations. These islands will grow laterally by step flow growth. Once the islands are large enough additional layers will begin to nucleate, and since adatoms must overcome an energy barrier to diffuse down a step a layered 3D structure, i.e. a hillock, will form [23].

In summary, the best material quality was achieved on 4° misoriented wafers at a growth temperature of 724° C in which case the growth rate (considered as optimal) was 85 µm/h. The surface morphology was smooth, hillock-free with 2-3 nm RMS roughness measured over a 5 by 5 µm AFM spot and with FWHM of the (004) reflection of XRD peak in the range of 20-30 arcsec [24].



(a) (b)

Figure 5. Growth on (100) GaP with 4° miscut towards (111)B (a); growth on plain "on-axis" (100) GaP (a) and on (100).

Other considerations, for example, those that describe the growth conditions that we have applied to reduce the undesirable IR absorption losses due to n-type charge carriers in the 2 - 4 μm range [25, 26] can be found in [27].

3.2.2. Growth on half-patterned GaP templates

A HP-template consists of every other stripe masked off with a 1 μm thick Si_3N_4 layer. Since HVPE is a near-to-equilibrium process the GaP will selectively grow on the unmasked stripe. This gives us the chance to study the behavior of the oriented domains separately, without their mutual interference. Patterning in two perpendicular directions—one perpendicular to the major and one perpendicular to the minor flat—according to the Zn-blended symmetry corresponds exactly to the opposite crystallographic orientations, i.e. a 90° rotation around [001] is equivalent to flipping from [001] to [00$\bar{1}$].

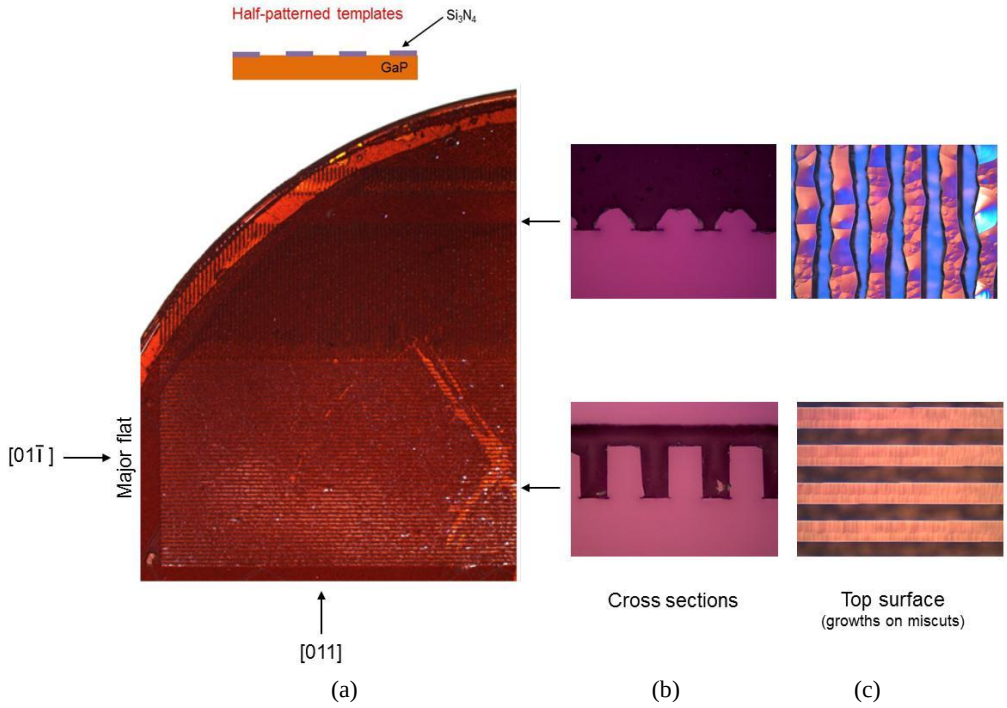


Figure 6. A HP-template with patterns along [01$\bar{1}$] and [011] (a); cross sectional (b); and top surface (c) images after HVPE growth.

The growth experiments conducted on "on-axis" HP-templates indicated that the growth on stripes oriented along [01$\bar{1}$] result in rectangular shaped mesas bounded by {110} and {100} planes, whereas the [011] oriented patterns formed triangular or trapezoid mesas bounded by {111} and {100} planes. The growth in [01$\bar{1}$] orientation was faster, 47 μm/h, but still comparable with the growth on the second orientation [011], 44 μm/h (Fig. 6-b). The shapes of the domain mesas remained about the same when the growth was performed on patterns developed on samples with 4° miscut. However, the growth rate for the [01$\bar{1}$] domains sharply increased to 78 μm/h, compared to only 47 μm/h for the [011] domains. Although that for 4° misoriented sample the two oppositely oriented domains grow with quite different rates, the [01$\bar{1}$] oriented pattern deposited on a 4° misoriented substrate seems to be best case in point of view of growth rate and mesas shape. In addition, this is the only orientation where the top surface of the domains remained hillock-free (Fig. 6-c) similar to the growth on plain misoriented substrates. An 8-hour long experiment was performed on such a template that resulted in 470 μm thick HP structure with rectangular shape of the domains and smooth hillock-free morphology. Thus the concept that GaP can be successfully grown on, generally, patterned templates was proven.

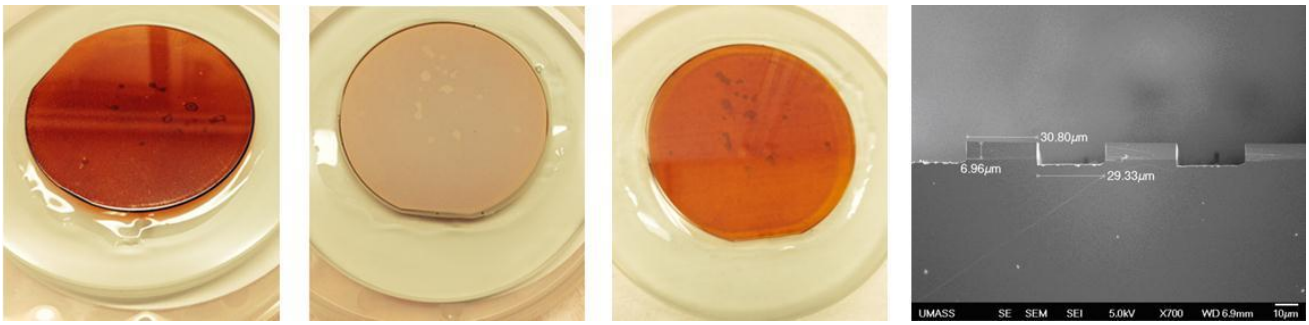
Although these results were in a good agreement with previously reported data for similar GaAs structures [28, 29] (more discussions on the mesas shapes are given in [30]), they did not answer unambiguously the question: "Which is the best orientation for patterning of the OPGaP templates?"

3.2.3. Preparation of the OP templates

The growths on HP-templates significantly contributed to the improvement of OP template preparation process. There are two major OP-template preparation techniques described in [26] for the case of OPGaAs. The first one is an entirely MBE-based process where the orientation of the polar layer (GaAs, GaP) can be changed using a non-polar lattice matched buffer layer. In the case of GaAs Ge is used, whereas in the case of GaP Si is used. Using this approach a GaP [00$\bar{1}$]/Si/GaP [001] structure is produced then patterned using photolithography and etched... This technique is precise but requires expensive MBE equipment. In addition, Si can contaminate a MBE system. The second technique, the wafer bonding technique, starts with bonding of two wafers with opposite crystallographic orientations at a temperature high enough to allow diffusion. After this step most of the upper layer must be polished off leaving only a few microns. The rest of the steps are the same— patterning using photolithography and etching. Although this technique does not require an expensive MBE reactor and sounds like "in-house" efforts, it still does require good polishing equipment and an experienced polisher that can ensure uniform thickness of the inverted layer. The wafer bonding of GaAs has a great advantage, because before bonding one can deposit a thin AlGaAs or InGaAs layer on one of the pieces, then capsulate this thin layer with another thin GaAs layer with precisely controlled thickness. After the wafer bonding and polishing, the rest of the GaAs material is etched off by a chemical that does not attacks the AlGaAs (or InGaAs) layer. Then the etch-stop layer is etched with a selective etch leaving the GaAs layer underneath. Thus thickness uniformity of the inverted GaAs layer is secured. The rest of the steps are the same— patterning using photolithography and etching.

Figure 7. Steps in the GaAs wafer bonding process—the presence of an etch stop layer secures the uniformity of the inverted layer, but still requires a MBE reactor.

Unfortunately, there is no suitable etch stop layer for GaP and removing the top wafer down to few microns is a challenging effort... In spite of lack of an etch stop layer, high quality wafer-bonded OPGaP templates were fabricated (Fig. 8) "in-house" using 2-inch "on-axis" (100) GaP wafers.



(a) (b) (c) (d)

Figure 8. Some of the steps in the GaP wafer-bonding process: Just bonded wafers (a); Top wafer lapped down to 20 µm (b); Top wafer polished down to 12 µm (c); Cross section of a wafer-bonded GaP template (d).

Several 3-inch MBE assisted GaP templates with domains perpendicular to the major flat (considered as the optimal orientation—see §3.2.2) with different pattern periods were also prepared by a collaborator (Fig. 9) using 3-inch (100) GaP with 4° miscut towards (111)B.

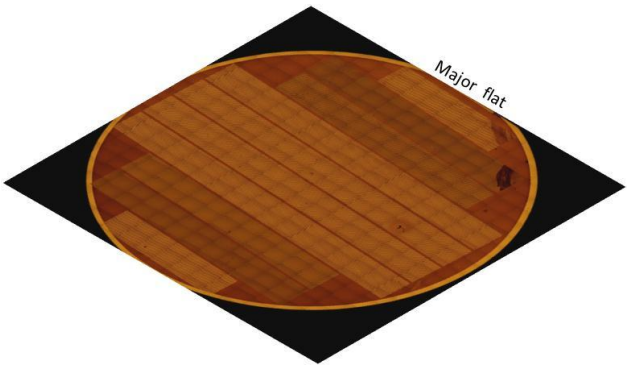


Figure 9. Three-inch MBE assisted OPGaP templates fabricated at BAE Systems.

It turned out that fabricating MBE templates on "on-axis" (100) GaP or on wafers with any other miscut is not possible. Thus, with a pattern on a MBE template oriented in the [01$\bar{1}$] direction (Fig. 6) we had not to worry much about hillock growth. However, we still had to deal with the very different growth rates of the two opposite orientations (see §3.2.2). The question "which pattern orientations and miscuts are suitable?" in case of wafer bonding templates also lost its sense as far as it turned out that we can bond successfully only "on-axis" templates. Then the remaining issue was not the difference in the growth rates, but the interactions of the propagating domains with the intensive hillock growth. A surprising result in the case of wafer-bonded templates was that the more favorable pattern orientation is not the one that is perpendicular to the major flat, but the one that is parallel.

3.2.4. Growth on oriented-patterned GaP templates

Initially, the growth experiments were performed on wafer-bonded templates because MBE-assisted templates were not available yet. Initial efforts were focused on short, 1-2 hour long experiments to establish growth conditions that provide high crystalline quality and retain the OP template pattern. We found that these conditions were different that those previously established for growth on plain GaP. Gradually the quality of OPGaP was improved for 1-hour long experiments (Fig. 10):

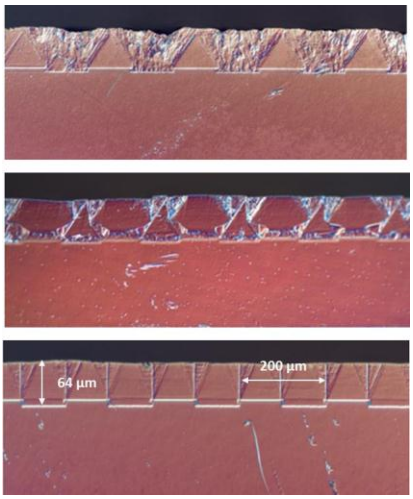


Figure 10. Progress in improvement of the domain fidelity in 1-hour long growths on OPGaP templates.

The hillock issue was also investigated [27]. It was found that hillocks often span several domains without disrupting the pattern. The domains continued to grow but just like in the case of HP-templates the hillock growth was more pronounceable when the domains were oriented along [011] and less in the direction [01$\bar{1}$], when growth on the pattern sometimes was even near hillock-free. Conditions to flatten and widen the hillocks were also established.

With the success achieved during short growth runs and improved templates the duration of growth on OP-templates was also increased. The initial result was that the domains survived for about 2 hour (120 μm) of growth and after that the pattern was overgrown.

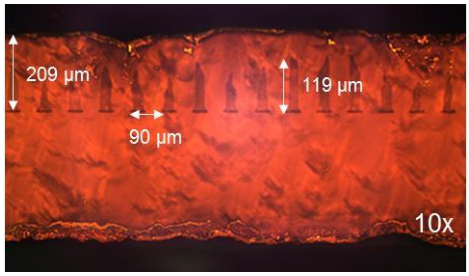


Fig. 11. Growth on a MBE (100) OPGaP template with 4 degree miscut towards (111)B

At the same time the growth surface was found to get rougher and sometimes was covered with etch pits. The later effect usually occurred after the 4th hour of growth when parasitic nucleation starts on the quartz dump tube and on the nozzle end in the mixing zone. Once the competitive parasitic nucleation starts before the precursors reach the substrate, the gas phase chemical composition changes uncontrollably varying the V/III ratio during the deposition. Due to these uncontrollable changes there may be an excess of HCl in the gas phase etching back the already grown layer. Avoiding this and some other undesirable effects (for instance the thermal inertness of the furnace, the influence of the back phosphine pressure when the cold trap is nearly full, etc.) resulted in much higher quality of the HVPE grown OPGaP layer with good domain fidelity and thickness increase. The maximum thickness of OPGaP to date is about 400 μm achieved reproducibly in one step growth in 8-hour long experiments:

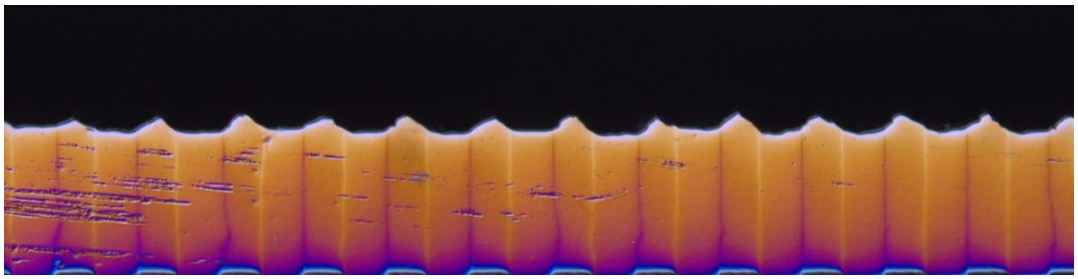


Figure 12. HVPE grown OPGaP—thickness up to 400 μm with good domain fidelity was achieved in one step growth.

This thickness of the OPGaP is nearly enough for laser pumping. Several samples are already prepared for some specific optical characterizations that eventually should lead to the demonstration of frequency conversion in OPGaP.

4. STUDY OF NEW MATERIALS AND FUTURE DIRECTIONS

The current trends in the market change as well the clients' requirements. The example given in §1 about the advance in the heat seeking missiles development is typical but not the only one. The needs for high power tunable and reliable portable IR and THz laser sources with no doubts are now urgent. That is why we are constantly researching new promising nonlinear materials. The coefficients of the nonlinear susceptibility, the width of the IR transparency, the 2PA coefficients, the thermal conductivity and the bandgap are the criteria to decide how suitable a material may be for nonlinear optical applications. The maturity and the diversity of the available growth approaches and template preparation techniques are always under consideration. For example, now we have the readiness to start growth experiments with III-Nitrides, more specifically GaN, which already has briefly attracted the scientific attention [31] as a promising QPM material. Although that the nonlinear susceptibility of GaN is not as high as GaAs and GaP (but still comparable to the one of $LiNb0_3$,) GaN has the advantages: wide bandgap, high thermal conductivity, mature HVPE technique for fast growth of thick layers, and several well developed techniques for patterned template fabrication.

In the last 1-2 years we have initiated hydrothermal growth of ZnSe single crystals. The intention is to use these crystals for fabrication of wafer bonded OPZnSe templates. (001). Solubility of ZnSe at different temperatures has been determined and was found suitable for thick growth (Fig. 13-a). As a second step we tried to optimized growth on (001) ZnSe by manipulating the temperature and the mineralized concentration. Temperature ranges 330-350ºC and 290-330ºC were examined. It was found that the higher temperature range (330-350ºC) results in fast growth but poor surface morphology such as growth hillocks and voids (Fig 13-b). In contrast, the lower temperature range (290-330ºC) occurred at slow growth (15-30 µm/day) but provided good surface morphology (Fig 13-c). It was also found that the presence of the growth hillocks can be mitigated by adding additional 2.5M of alkali chloride to the 5M NaOH mineralizer in the solution, which stimulates the growth rate in (111) direction and thus improve the uniformity of the crystal along (001). Further adjustments aim to achieve high quality growth of (001) ZnSe at a growth rate that will result in 2-2.5mm thick samples in about 30 days of continuous growth.

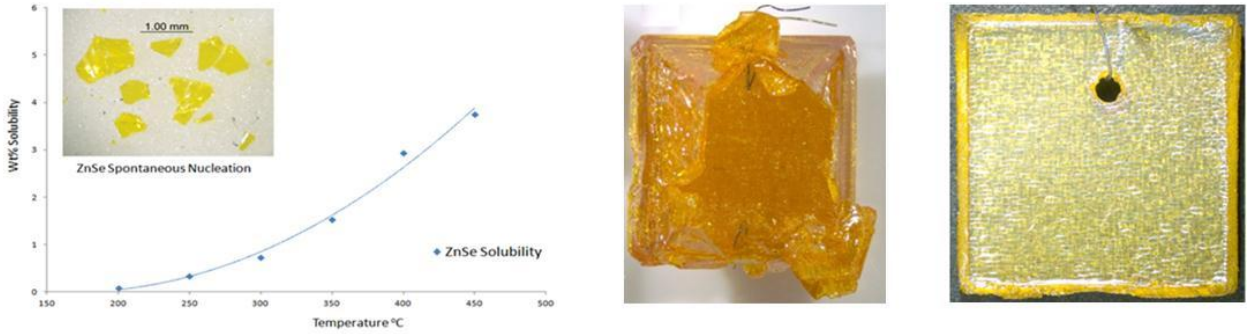


Figure 13. Solubility data of ZnSe in 5M NaOH between temperatures ranges of 200 and 450 ºC (a); ZnSe crystal grown using 5M NaOH/2.5M NaCl mineralizer and a temperature range of 340 to 350ºC showing growth hillocks and voids (b); ZnSe crystal grown using 5M NaOH/2.5M NaCl mineralizer and a temperature range of 300 to 325ºC showing a smooth and even (001) growth orientation (c).

ZnTe is another promising, similar to ZnSe, II-VI nonlinear optical material, which nonlinear properties and 2PA, according [33] are even better for some frequency ranges. This could be another destination in this interesting scientific journey.

5. DISCUSSION AND CONCLUSSION

The quasi phasematching approach for conversion of frequency in the mid-IR and THz regions require nonlinear optical materials with high nonlinear susceptibility, wide bandgap and low two-photon absorption in the pumping range. At least 400-500 µm thickness of the structure with oppositely oriented domains with good domain fidelity is necessary in order to allow beam propagation and wave- mixing processes. The efforts described here were focused on development of several different nonlinear materials with a focus on, GaP. The progress in both the development of the wafer preparation techniques and the improvement of the subsequent thick HVPE growth on these OP-templates are described. For example a strategy how to optimize the growth conditions is given. The discrepancy between the optimal growth conditions determined by other authors and ours are attributed to the importance of the reactor configuration and the local micro-events that happen on the growing surface and in the gas stream. Some typical problems that appear only at experiments longer than 4-8 hours and the routine ways to solve them are also discussed. No matter the high sensitivity of the process to small changes in the experimental conditions, we claim that the quality and the parameters of the grown materials are highly reproducible when the optimal conditions and proper process procedures are captured once. An idea for the future direction in this research can be seen in the text. Characterizations not described here and progress beyond the one shown will be revealed in near future.

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